Effect of Water on the Potential of the Glass Electrode.[1]

By Hisato YOSHIMURA.

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Since Haber and Kremensiewicz[2] set forth the hypothesis that the water absorbed by the glass membrane of a glass electrode transforms it into a hydrogen electrode, its importance has been in general implicitly recognized. No experimental studies on this point have been reported, however, except that of Laug[3], who found that, on drying the surface of one side of the electrode membrane, the hydrogen electrode function of that surface decreased and its potential level against that of the other side rose. He attributed the phenomenon to the decreased permeability of the hydrogen ion through the glass phase. The interrelation between the two facts was proved, however, neither theoretically nor experimentally. The aim of the present study is directed to these points.

The dotted line indicates the paraffin layer. The bulb part of the electrode is made either of MacInnes glass or of commercial glass, while the capillary support is always of commercial soft glass. On the details of the use of this electrode, see the previous report[4].

Fig. 1.

Experimental.

Glass electrodes made of MacInnes glass and also of commercial glass were used, the form of which is sketched in Fig. 1. The potential was measured at 25°C. with a Lindemann electrometer. The sign of the value given in this paper refers to the inside of the bulb of the electrode which serves as the electrode membrane.

(a) Experiments on the effect of submerging the glass electrode in water. After a glass electrode was prepared, it was preserved in water. Measurements of its asymmetry potential (usually in a buffer solution of *p*H 7.3), the hydrogen electrode function, the error of glass electrode

(1) Studies on the Nature of the Glass Electrode Potential. II. I: *J. Biochem.* (Japan), **23** (1936), 91.

(2) Haber and Kremensiewicz, *Z. physik. Chem.*, **67** (1909), 385.

(3) Laug, *J. Am. Chem. Soc.*, **56** (1934), 1034.

(4) Yoshimura, *J. Biochem.* (Japan), **21** (1935), 335.

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(defined by Dole[5]) in an alkaline solution of pH 10.9 (its sodium ion concentration being 0.1 mol), and the degree of corrosion of the glass membrane due to water were repeated daily. The hydrogen electrode function, here stated, is the change in the potential of a glass electrode corresponding to the unit change of pH of the solution, and is expressed by $\Delta E/\Delta p$H. Estimations were made over a range of pH 2–7, where a rectilinear relationship exists between the potential and the pH. The degree of corrosion of the glass membrane due to water was examined by the following way: a 0.0001 N hydrochloric acid solution containing 0.001% methyl red was placed in the bulb of the glass electrode including a small air bubble. The electrode being rotated in a bath of 50°C., the time required for the fading of the red colour in the solution was measured. Measurements, being repeated on different days, indicate the relative degrees of corrosion by water on those days.

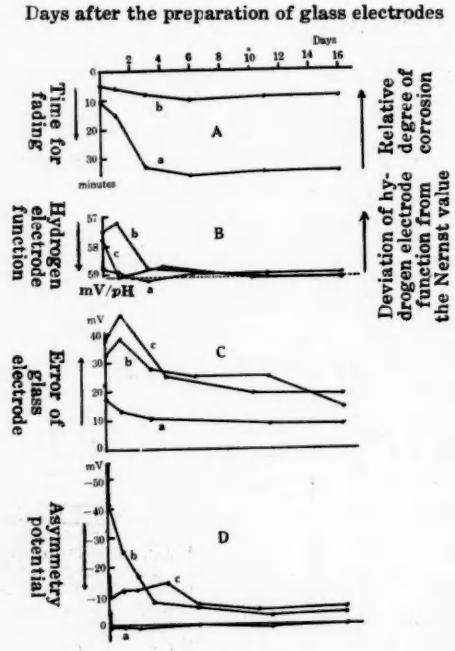

Fig. 2.

The above-mentioned examinations were carried out on a number of electrodes, examples of which are given in Fig. 2. The results of two electrodes made of MacInnes glass are given by curves a and b and those of an electrode of commercial glass by curves c. As is seen in A, the corrosion of the glass membrane decreased day by day and finally it attained a constant value after being submerged for about a week, when an equilibrium between the glass surface and the water was presumably attained. Similarly, the deviation of $\Delta E/\Delta p$H from the Nernst value (indicated by the dotted line) (B) and the error of glass electrode in the alkaline solution (C)

(5) Dole, *J. Am. Chem. Soc.*, **53** (1931), 4260.

decreased day by day and the asymmetry potential (D) approached zero from a negative value, each finally attaining a constant value.

The time required for the potential equilibration after the electrode was mounted in the solution was shortened by first submerging the electrode in water after its preparation.

(b) Experiments on the effect of drying the surface of electrode membrane. Further to clarify the relationship of water to the potential of a glass electrode, the effect of drying one surface of the electrode membrane was examined. The surface was dried either by passing through hot air (1) or by means of a desiccator (2).

(1) A commercial glass electrode which had attained the equilibrium with water was dried on one side, either inner or outer, by passing hot air of ca. 180°C. through or over it for about 6 hours, while the other side was prevented from drying by passing vapour or hot water through or over it. The asymmetry potential and $\Delta E/\Delta p$H were examined before and shortly after drying. After the examinations were completed, the electrode was preserved in water and the electromotive reactions of the electrode were observed to determine the effect of the immersion on the potential. An example of the results is given in Fig. 3, where A gives the asymmetry potential and B gives $\Delta E/\Delta p$H of the dried surface. The shadowed range represents the time of drying. The effect of drying the inner surface of an electrode is represented by continuous lines (electrode 1), while that of drying the outer surface of another electrode is shown in broken lines (electrodes 2 and 3). As is seen in the figure, drying changes the asymmetry potential by raising the potential level of the side of the dried surface, while it decreases $\Delta E/\Delta p$H on the same side. When the electrode was submerged in water after this drying experiment, this effect on the potential was reversed. Though it is doubtful whether the effect of the passage of hot air on the potential is completely due to the evaporation of water from the glass

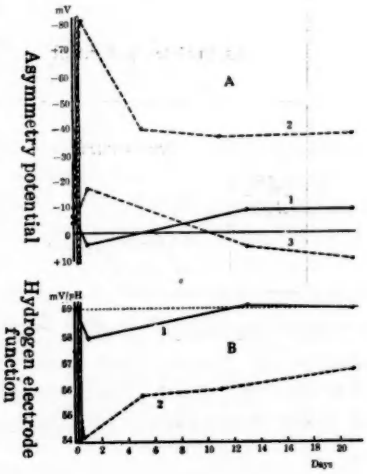

Fig. 3.

surface, drying seems to play an important rôle, as the reverse effect was produced by submerging it in water.

(2) The electrode which was equilibrated in water being connected with a sulphuric acid desiccator, its inner surface was dried for 8 days, while the outer surface was kept submerged in water. The asymmetry potential (in a buffer solution of pH 2.8) and $\Delta E/\Delta p$H before and after drying are given in Table 1, where m refers an electrode of MacInnes glass, and c that of a commercial glass electrode. The effect of drying on the asymmetry potential was similar to that found in the experiment (1), while the change in $\Delta E/\Delta p$H by drying was minute in this case.

Table 1.

			Before desiccation	After desiccation
Asymmetry potential		m	−11.5 mV	− 1.2 mV
		c	−27.4	− 5.8
$\frac{\Delta E}{\Delta p\text{H}}$	Inner surface	m	58.7 $\frac{\text{mV}}{p\text{H}}$	58.3 $\frac{\text{mV}}{p\text{H}}$
		c	58.7	57.3
	Outer surface	m	57.6	58.0
		c	57.5	58.2

The attainment of the equilibrated potential after the electrode was mounted in the solution was retarded if measured shortly after the electrode was dried. But when the electrode was submerged in water for a few days, this effect disappeared.

Discussion.

From the above experimental results, it is clear that, water being removed from one surface of the electrode membrane, the $\Delta E/\Delta p$H on that surface is decreased and the potential level is raised on that side against the other, thus causing a change of the asymmetry potential. These changes in the electromotive effect of the glass membrane can be reversed by submerging the electrode in water, probably because water is absorbed in the glass surface. The asymmetry potential is created by the differences in electromotive effect between the surfaces of the electrode

membrane. Thus the change in the asymmetry potential from a negative value to zero when a freshly prepared electrode is submerged in water (refer to D of Fig. 2) is due to the fact that the effect of water on the outer surface is more severe than that on the inner surface. Thereby the electromotive effect of both surfaces is equalized by water.

While the reason for this difference between the inner and the outer surfaces is a matter for further study, the correlation between the asymmetry potential and $\Delta E/\Delta p\mathrm{H}$ can be explained qualitatively by three current important theories of the glass electrode: Dole's statistical mechanical theory[6], the partition potential theory by Gross and Halpern[7], and the ion exchange theory of Horovitz[8], all belonging to the phase boundary theory. No experimental results have yet been produced to support one against the other two, so that these three theories are taken into consideration.

In all of these theories, the phase boundary potential E is given by

$$E = -\frac{RT}{F}\ln C_{\mathrm{H}}\left\{1+\frac{C_{\mathrm{Na}}}{C_{\mathrm{H}}}\frac{Y}{X}\right\}^{n}-\frac{RT}{F}\ln X \qquad (1),$$

E being positive when the potential level of the solution is high against that of the glass phase. C_{H} is the hydrogen ion concentration (strictly the hydrogen ion activity) of the solution and C_{Na} the sodium ion concentration (the cation of the salt in the solution being assumed to be Na^{+}). n is 1 in both Dole's and Horovitz's theories, and is $\frac{1}{2}$ in Gross and Halpern's theory. X and Y are the constants which depend upon the nature of glass or, strictly speaking, upon that of the membrane surface, and are given as follows:

$$X = \beta_{\mathrm{H}}e^{\frac{Q_{\mathrm{H}}}{RT}}, \quad Y = \beta_{\mathrm{Na}}e^{\frac{Q_{\mathrm{Na}}}{RT}} \quad \text{(Dole)},$$

$$X = \frac{K_4M_4}{K_1L_4}\sqrt{\frac{L_1}{M_1}}\times\text{const.}, \quad Y = \sqrt{\frac{M_1}{L_1}}\times\text{const.} \quad \text{(Gross and Halpern)},$$

$$X = \frac{u_{\mathrm{H}}}{aK_{\mathrm{H}}u_{\mathrm{Na}}}, \quad Y = \frac{1}{aK_{\mathrm{Na}}} \quad \text{(Horovitz)}.$$

(6) Dole, *J. Chem. Phys.*, **2** (1934), 862.

(7) Gross and Halpern, *Z. physik. Chem.*, **115** (1925), 54; *J. Chem. Phys.*, **2** (1934), 136.

(8) Horovitz, *Nature*, **127** (1931), 440.

Various symbols in these equations are the constants which are independent of one another. On their physical meanings, refer to the original papers.

From the equation (1), the asymmetry potential e_g and the hydrogen electrode function $\Delta E/\Delta p\mathrm{H}$ are given as follows:

$$e_g = \frac{RT}{F} \ln \left\{ \frac{1+\frac{C_{Na}}{C_H}\frac{Y_o}{X_o}}{1+\frac{C_{Na}}{C_H}\frac{Y_i}{X_i}} \right\}^n + \frac{RT}{F} \ln \frac{X_o}{X_i} \qquad (2),$$

where the suffixes i and o refer to the inner and the outer surfaces of the electrode membrane respectively, and

$$\frac{\Delta E}{\Delta p\mathrm{H}} = \frac{R'T}{F}\left\{1 - \frac{\log\left(1+\frac{C_{Na}}{C_H}\frac{Y}{X}\right)^n}{\Delta p\mathrm{H}}\right\} \qquad (3),$$

where R' represents $2.303R$.

Before using these equations to explain the experimental results, the two following points should be discussed: (i) It is noticeable that, according to these theories, the only way to explain the deviation of $\Delta E/\Delta p\mathrm{H}$ from the theoretical value $(R'T/F)$ is by the cation effect, i.e. by the term $\frac{C_{Na}}{C_H}\frac{Y}{X}$ in the equation (3). This term is generally thought to be negligible in solutions of pH lower than 8. Moreover, it is a function of C_H and C_{Na}. The deviation of the experimental values of $\Delta E/\Delta p\mathrm{H}$ from the theoretical is, however, approximately a constant at least in the range of pH 2–8. Therefore, it is a matter of question whether or not the deviation of $\Delta E/\Delta p\mathrm{H}$ from the theoretical value can be explained by the cation effect. From these points, Kahler and DeEds[9] offered the deviation film theory apart from the cation effect to explain the deviation of $\Delta E/\Delta p\mathrm{H}$. This theory has, however, already been denied by the present author[1] who maintains that the magnitude of the hydrogen electrode function is closely connected with the property of the glass surface. Then the question being left to further study, the equation (3) will be adopted provisionally in the present discussion to explain the deviation of $\Delta E/\Delta p\mathrm{H}$ from the theoretical value. (ii) All these theoretically derived equations refer to the equilibrated potential, while

(9) Kahler and DeEds, *J. Am. Chem. Soc.*, **53** (1931), 2998.

the potential observed experimentally showed the diurnal change. Regarding the observed potential be in a state of the quasi-equilibrium, these equations can be said to apply, and the diurnal change of the potential can be explained by the change in the constants in the equations.

Now, from the equations (2) and (3), it is clear that when the constant X of one surface of the electrode membrane is decreased $\Delta E/\Delta p\mathrm{H}$ on that surface decreases and the potential level on that side rises, causing the change of the asymmetry potential, and vice versa. The fact is corroborated by the experiments.

From the equation (1), the error of the glass electrode in an alkaline solution (designated by Δ) is given by the equation

$$\Delta = \frac{RT}{F} \ln \left\{1+\frac{C_{\mathrm{Na}}}{C_{\mathrm{H}}} \frac{Y}{X}\right\}^n \qquad (4).$$

Thus the decrease in Δ is accompanied by the increase in $\Delta E/\Delta p\mathrm{H}$. This is the fact which was found in most cases of the experiment (a).

As the level of the potential on one side of the membrane falls and $\Delta E/\Delta p\mathrm{H}$ increases when the surface of the membrane on that side is corroded with water, it must be that the constant X is increased by water corrosion, and decreased by drying. The physical meaning of this change in X can be explained separately by each of the above-mentioned three theories. For example, according to Gross and Halpern's theory, the increase of X by water corrosion can be explained by the increase in the partition coefficient of water in the glass phase; and according to Dole's theory, it is explained by the decrease in energy of the hydrogen ion on the lowest quantum level in the glass phase or by the increase in that of sodium ion.

Thus we can explain qualitatively our experimental findings by current theories of the glass electrode. It is impossible, however, to say which of the three theories is correct.

Summary.

(1) When one surface of the membrane of a glass electrode is dried, the asymmetry potential is raised on that side against the other side, and the hydrogen electrode function is decreased. This membrane being kept submerged in water, the reverse effect is observed. These facts can be explained qualitatively by any of the latest theories concerning the glass electrode.

(2) The significance of preserving the glass electrode in water after its preparation, which is a generally accepted procedure in the use of the glass electrode, can be stated as follows: (i) It makes the hydrogen electrode function approach Nernst's theoretical value, probably decreasing the cation effect on the potential of the glass electrode, (ii) it decreases the asymmetry potential, equalizing the electromotive nature of both the inner and outer surfaces of the electrode membrane, and (iii) it facilitates the equilibration of the potential after the electrode is mounted in a solution for test.

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On the Silver Oxide Positive of the Alkaline Accumulator. II.

By Kyôji KINOSHITA.

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The author reported some experimental investigations on the general features of the silver oxide positives of alkaline accumulator.[1] The present report describes the further experiments, the detailed description[2] being published in Japanese.

In the previous paper, the author pointed out that the chemical reactions corresponding to the discharge of the positives are

$$Ag_2O_2 \rightarrow Ag_2O + \frac{1}{2}O_2 \rightarrow 2Ag + \frac{1}{2}O_2 \qquad (1).$$

It has also been found that the coefficient of utility of the active material and the capacity of the positive electrode are higher than those of the

(1) Kinoshita, this Bulletin, **12** (1937), 164.
(2) Kinoshita, *Toyoda Kenkyu Iho*, **4** (1936), 116-141.

lead peroxide positive of the lead acid cell. In order to bring out the cause of these special features of the silver positive, further experiments have been done, especially on the charging characteristic of the positive.

Experimental. (a) Amount of Oxygen Fixed in the Active Material, and the Discharge Capacity of the Positive. Silver oxide positives were prepared by applying silver oxide paste to the grid as stated in the previous paper. The grid was made of iron plated with silver, the size being about $5.8 \times 1.6 \times 0.25$ cm. "Formation" of the positives was continued for about 17–21 hours by a current of 60 milliamperes.

Fig. 1 shows the construction of the cell. A is a glass vessel of H-shape, P a silver oxide electrode, and N a negative electrode of the "Nife" accumulator. The amount of gas evolved at the positive P was measured by collecting in a glass cylinder G through the tube B. The total amount of electricity, K', passed for charging the cell was measured by means of a copper coulombmeter connected in series to the cell. Nine cycles of discharges were made on the cell. The results are summarized in Table 1.

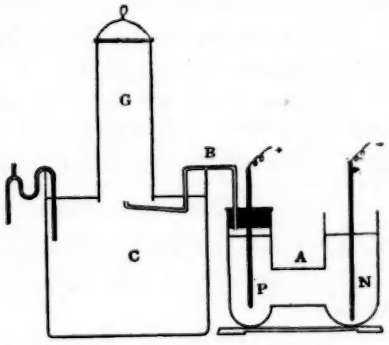

Fig. 1.

Table 1. Comparison of K and C.

Number of cycle	Total amount of elect. used for charging (K') (A.H.)	Volume of gas evolved (0°C., 1 atm.) (c.c.)	Amount of elect. as a loss (K'') (A.H.)	$K = K' - K''$ (A.H.)	Discharge capacity (C) (A.H.)
1					2.080
2	9.30	1506	7.21	2.09	2.030
3	7.80				2.115
4	3.17	394	1.89	1.28	1.260
5	1.89	170	0.81	1.08	1.065
6	1.60	93.7	0.45	1.15	1.149
7	1.72	105	0.50	1.22	1.200
8	1.80	140	0.67	1.13	1.125
9	1.69	122	0.58	1.11	0.949

In the 3rd and 4th columns of the table, the total volume of the gas evolved at P and the amount of electricity (K'') corresponding to the volume of gas are tabulated respectively. The values $K = K' - K''$ in the table are considered to represent the amount of electricity consumed in oxidizing the active material in the positive. The values of K are in good coincidence with the discharge capacity C in the succeeding discharge. This may lead to the consideration that the entire amount of oxygen fixed in the active material of the positive in the charge, may be consumed in the succeeding discharge.

In the case of the 1st discharge in Table 1, for example, K' amounted to 9.30 ampere-hours, and if K' be used only for the electrolysis of water, the amount of oxygen which will be evolved at P is calculated to be 1946 c.c. at 0°C. and 1 atm. So that the volume of oxygen which was fixed in the active material in the charge will be

$$1946 \text{ c.c.} - 1506 \text{ c.c.} = 440 \text{ c.c.} \quad (0°\text{C.}, 1 \text{ atm.}).$$

On the other hand, the electrode used contains 5.08 g. of Ag_2O as an active material, accordingly, the amount of oxygen in the electrode may be as follow:

$$22400 \times (5.08 \times O_2/2\,Ag_2O) \times (1/O_2) = 245 \text{ c.c.} \quad (0°\text{C.}, 1 \text{ atm.}).$$

The amount of oxygen which is expected to exist in the positive considering the charged active material to be Ag_2O_2 will be $245 \times 2 = 490$ c.c. (0°C., 1 atm.). From these calculations, it can be concluded that the active material of the plate, in charged state, is composed of a silver oxide of a higher degree of oxidation than Ag_2O. The same result was already described in the preceding paper.

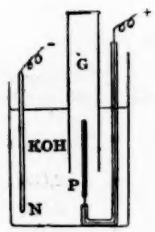

Fig. 2.

In the above experiments the grids made of iron were used for the preparation of the positive. By the use of such a grid, however, the discharge capacity of the positive diminishes gradually as the cycles of discharge are repeated. So in the following experiments the grids of lead-antimony instead of iron was used. In this case the positive P was fixed in a large vessel A, as shown in Fig. 2. N is a negative electrode, and G a glass cylinder for collecting the gas evolved at P. The results are tabulated in Table 2. The same conclusion can be obtained from this table as from Table 1.

Table 2. Comparison of K and C.

Number of cycle	Total amount of elect. used for charging (K') (A.H.)	Volume of gas evolved (0°C., 1 atm.) (c.c.)	Amount of elect. as a loss (K'') (A.H.)	$K = K' - K''$ (A.H.)	Discharge capacity (C) (A.H.)
1					2.242
2	3.363	330.2	1.58	1.78	1.780
3	2.376	142.2	0.68	1.70	1.634
4	2.450	144.0	0.69	1.76	1.750
5	2.750	204.0	0.98	1.77	1.759
6	2.708	178.9			

(b) Changes of the Rates of Gas Evolution in the Course of Charge. Rates of gas evolution at a silver oxide electrode in the course of charges were measured. Fig. 3 shows an example of the results obtained. In the figure the ordinate indicates the velocity of gas evolution (c.c./min.) or the terminal voltage of the cell (volts), and the abscissa the time of charge and discharge (min.). The curve represented by circlets shows the evolved gas, and the curves represented by black dots are the characteristic curves of the cell in charge and discharge, the current being taken as 500 milliamperes. The terminal voltage of the cell in charge rises abruptly at about 75 min., accompanied by a slow evolution of gas. The rate of gas evolution rose slowly, and at last it reached nearly 1.74 c.c./min. The value 1.74 c.c./min. coincides with theoretical rate of gas evolution at the positive electrode in the electrolysis of water by the current of 500 milliamperes. So that the curve is considered to indicate the change of rate of propagation of oxidizing reaction at the electrode, and the reaction proceeds no more when the rate of gas evolution reached 1.74 c.c./min.

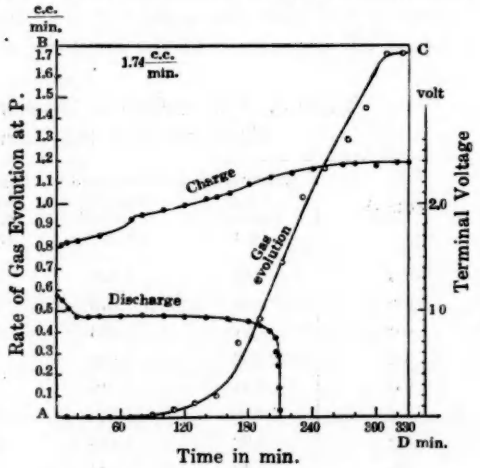

Fig. 3.

The area ABCD in Fig. 3 corresponds to the total amount of gas which will be evolved at the positive in the case of electrolysis of water by the current of 500 milliamperes in 330 min. The area surrounded by the straight lines AB and BC, and the gas evolution curve, corresponds to the amount of oxygen, which was fixed in the active material of the plates, and the rest, which lies on the right side of the curve indicates the amount of gas evolved at the positive as a loss.

(c) Proceeding of Oxidizing Reaction at the Electrode and the Amount of Electricity Used for Charging the Cell. Now, a very interesting special feature of the silver oxide positive was observed. The silver oxide positive in the pasted form could be discharged before applying any electrolytic treatment, i.e., "formation". The discharge capacity of the positive, in this case, almost coincides with those expected from the amount of silver oxide pasted in the positive and from the following chemical reaction:

$$Ag_2O \rightarrow 2Ag + \frac{1}{2}O_2 \qquad (2).$$

The calculated and the observed capacities are compared in Table 3. As seen in the table the coefficient of utility reaches from 90 to 97%. In this case the capacity S of the electrode may be considered to be the in-

Table 3. Comparison of Discharge Capacity at First Discharge with the Calculated Value.

Electrode	Amount of Ag_2O pasted (g.)	Discharge capacity (calc.) S (A.H.)	Discharge capacity (obs.) S' (A.H.)	Coefficient of utility (%)	Capacity per 1 g. of Ag_2O (mA.H./g.)
6 a	4.61	1.066	1.038	97.3	225
6 b	4.66	1.078	1.050	97.4	225
6 c	4.91	1.146	1.100	95.9	224
6 d	4.72	1.092	1.058	96.8	224
6 e	4.84	1.119	1.038	92.8	215
6 f	4.89	1.130	1.050	93.0	215
6 g	4.82	1.115	1.038	93.1	215
6 h	4.90	1.134	1.050	92.6	214
7 a	4.97	1.150	1.075	93.4	216
7 b	4.84	1.121	1.033	92.1	214
7 c	5.13	1.188	1.104	92.8	215
7 d	5.33	1.235	1.150	94.1	216

herent capacity of the electrode, which is to be determined by the amount of Ag_2O pasted in the grids.

In the following experiments the relation between the progress of the oxidizing chemical reaction at the electrode, and the amount of electricity used for charging the cell was examined. The degree of the oxidizing reacton at the electrode in charge can be measured from the discharge capacity of the cell in the succeeding discharge.

Four silver oxide electrodes were subjected to charge and discharge by the current of 250 milliamperes, and the values of K (which was measured from C in the succeeding discharge) was estimated, the values of K' being varied at the same time.

In Fig. 4 the values of C of the electrodes are taken in ordinate, and the K' in abscissa. As seen in the figure, if K' be smaller than 1.5 S_m[3], it is nearly equal to C in the succeeding discharge. In this case, there-

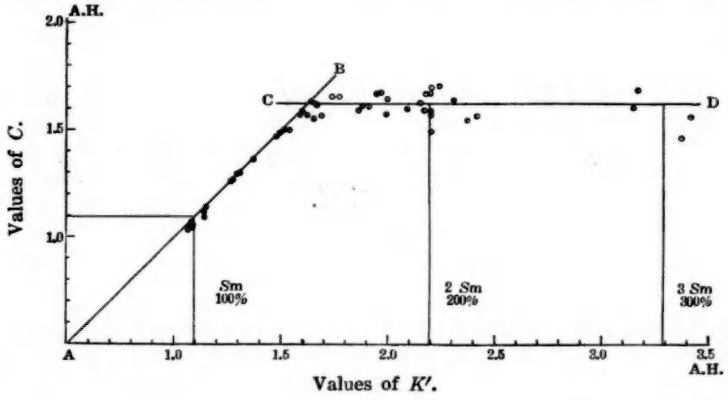

Fig. 4.

fore, we can forecast the end of the discharge by dividing K' by the magnitude of discharge current in the ranges of a few minutes. If K' be greater than 1.5 S_m, C becomes constant and nearly equal to 1.5 S_m.

The inherent capacity of the electrode S is the theoretical one, the fundamental chemical reaction of the electrode being assumed to be (2). Accordingly, it may be expected that the total capacity of the electrode will increase to as much as $2S$, if the active material of the electrode

(3) S_m means the mean inherent capacity of the four electrodes used in the experiments.

be oxidized into Ag_2O_2, as the result of repeating the cycles of charge and discharge.

Relations between K' and K (or C) were examined by varying the magnitude of the charging current. The results obtained are diagramatically represented in Fig. 5 and Fig. 6, which correspond to the data obtained by the charging current of 500 milliamperes and 1000 milliamperes respectively.

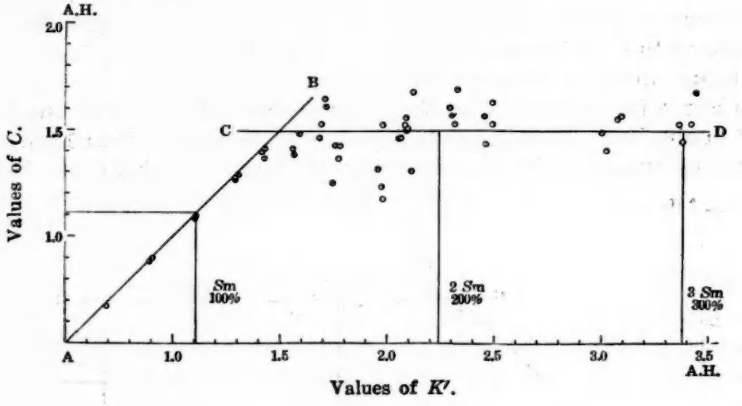

Fig. 5.

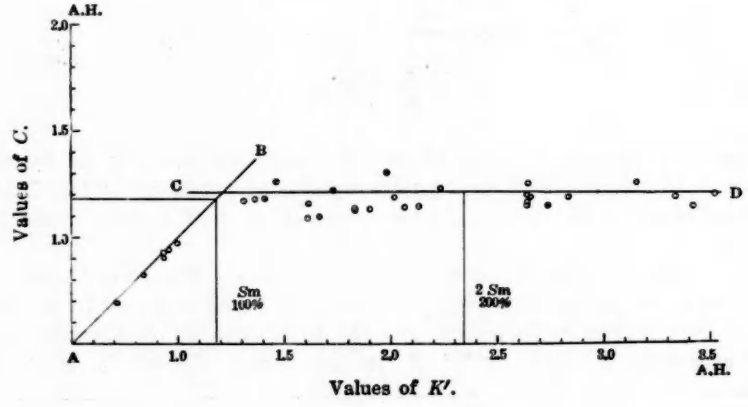

Fig. 6.

(d) Relation between Magnitude of Charging Current and Charged Amount of Electricity. As the result of experiments (c) it may be expected that the amount of electricity actually accumulated in the active material i.e., the amount of electricity consumed for oxidizing the active material of the electrode, changes with the magnitude of the charging current.

The silver oxide positives were charged fourteen times as much as their inherent capacities, the magnitude of the charging current in this case being from 100 milliamperes to 1300 milliamperes. And then they were discharged by a current of 250 milliamperes. The results thus obtained are summarized in Table 4.

Table 4.

Charging current (I) (ampere)	Time of discharge (t) (hours)	Discharge capacity (C) (A.H.)	log I	log t	log t (calc.)
0.100	6.471	1.604	−1.000	0.808	
0.200	5.566	1.392	−0.699	0.746	
0.300	5.750	1.438	−0.523	0.760	0.761
0.400	5.558	1.389	−0.398	0.745	0.744
0.500	5.383	1.346	−0.301	0.731	0.731
0.700	5.142	1.286	−0.155	0.711	0.711
1.000	4.892	1.223	0.000	0.688	0.690
1.300	4.725	1.181	0.114	0.675	0.675

The following tendency can be noticed from the table: the discharge capacities (C) of the electrodes become smaller with the increase of the charging current, but an especially small discharge capacity was observed when the charging current was 200 milliamperes. In the 4th and the 5th columns of the table, the values of $\log I$ and $\log t$ are tabulated. Plotting these values on a $\log I - \log t$ diagram, we obtain a straight line, as seen in Fig. 7. So that the relation can be represented by the following equations;

$$\log t = -n \log I + \log k \qquad (3),$$

$$I^n t = k \qquad (4),$$

where n and k represent constants. The equation (4) is analogous in form to Peukert's formula[4] which gives the relation between discharge

(4) Peukert, *Elektrotech. Z.*, (1897), 287.

hour rate and the magnitude of the discharge current in the lead acid storage cell. Two constants in the equations (3) and (4) were found to be $n = 0.136$, and $\log k = 0.690$. In the 6th column of the table, the values of $\log t$ calculated from the equation (4) are tabulated.

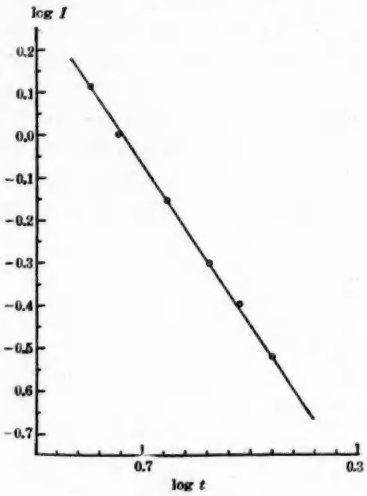

Fig. 7.

(e) On the Peptization of the Active Material at the Electrode. The silver oxide positives, in many cases, dispersed their active material into the solution of electrolyte when they were subjected to charge and discharge, forming a colloidal solution of silver oxide. This phenomenon was already noticed by Jirsa,[5] the author,[2] and Tanaka.[6] The colour of the colloidal silver observed in these experiments[7] was sometimes pink, yellow, brown, bluish brown or black. In order to see the effect of the concentration of the electrolyte upon the formation of the colloid, two electrodes (4H and 4I) were charged and discharged by a current of 100 milliamperes. The result observed at their first charge is summarized in Table 5. As seen in the table the formation of the colloid seems to have some relation to the concentration of the electrolyte. From

Table 5.

Electrode	Conc. of electrolyte	Colour of colloid	Remark
4 H	40% KOH	Pink	Upper part of the electrolyte: pink; lower part: transparent.
4 G	2.5% KOH	Dark yellow	Upper part of the electro'yte: transparent; lower part: dark yellow.

(5) Jirsa, *Z. Elektrochem.*, **33** (1927), 129.

(6) Tanaka, *J. Electrochem. Assoc. Japan*, **3** (1935), 9.

(7) The photographs showing the formation of the colloids can be seen in the original paper (2).

the second charge onward the formation of the colloid in pink colour cannot be observed even in the case of electrode 4 H.

Positive and negative electrodes of the cell were put into two separate glass vessels, each containing 20% KOH solution, and the vessels were connected with a U-tube, which was also filled with 20% KOH solution. The charging current of this cell was taken to be 100 milliamperes, the peptization of the active material could be noticed only in the electrolyte into which the silver oxide positives were dipped. In discharging the positives, formation of the colloids could also be observed.

Consideration of the Results. The fundamental chemical reactions involved in the charge and discharge of the silver oxide positives will be considered to be as follows:

$$Ag_2O_2 \rightarrow Ag_2O + \frac{1}{2}O_2 \rightarrow 2Ag + \frac{1}{2}O_2 .$$

Of these the decomposing reactions of silver oxide into metallic silver corresponds to the discharge of the cell.

On the other hand, it was noticed, that the reduction of the active material occurred at first at the ribs of the grid, and then propagated into the inner part of the active material. This fact can easily be known from the colour difference between Ag_2O and Ag.[8] The material in discharged part is metallic silver, which is good electrical conductor, so that the discharge reaction will proceed smoothly and completely even in the innermost part of the active material.

In case of a charge, on the other hand, the active material in uncharged state (metallic silver) will be separated from the rib by a layer of charged material (silver oxide) which has small electrical conductivity. Accordingly the charging chemical reaction will not proceed so smoothly into the active material.

The following characteristic properties of the silver oxide positives may be explained from the above considerations: (1) Silver oxide positive gives very high values of coefficient of utility of the active material; (2) discharge capacities and the utility coefficient are not so seriously affected by the magnitude of the discharge current; (3) the oxygen fixed in the active material of the positives in a charged state is

(8) The photographs showing the propagation of chemical change at the electrode in discharge can be seen in the paper published in Japanese: Kinoshita, *J. Electrochem Assoc. Japan*, **4** (1936), 27; *Toyoda Kenkyu Iho*, **4** (1936), 108.

consumed completely in the succeeding discharge; (4) the amount of electricity charged in the active material is affected seriously by the magnitude of the charging current.

In conclusion, the author wishes to express his hearty thanks to Prof. J. Sameshima of the Tokyo Imperial University for his valuable advice.

Summary.

(1) Further experimental investigations were made on the charge and discharge characteristics of the silver electrode of the cell which was constructed from the silver positive and the iron negative in KOH solution.

(2) Silver oxide positive gives very high value of the coefficient of utility of the active material.

(3) Discharge capacity and the utility coefficient are not seriously affected by the strength of the discharge current.

(4) The oxygen fixed in the active material in the charged state is consumed completely in the succeeding discharge.

(5) The amount of electricity charged is affected seriously by the strength of the charging current.

(6) These phenomena can well be explained by the following chemical reactions.

$$Ag_2O_2 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} Ag_2O + \frac{1}{2}O_2 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} 2Ag + \frac{1}{2}O_2 .$$

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Catalytic Hydrogenation of Amides of α-Hydroxy-Acids (Continued).[1]

By Haruomi ÔEDA.

(Received July 24th, 1937.)

Experiments on the formation of 1,4-diamine and of 1,2-glycol from α-hydroxy-amide by catalytic hydrogenation in the presence of copper-chromium oxides, were extended to phenyl-lactamide.

From this amide benzyl-ethylene glycol and a solid base were obtained. The solid base, when fractionally recrystallized from alcohol, can be separated into two fractions, one of which melts at 142–144° (A) and the other at 166–167° (B). Results of analysis of both bases show that they correspond to the same diprimary diamine shown below, i.e. they are isomeric with each other.

On benzoylation, the latter base (B) gives a derivative melting at 280–282° (*Bz*.B) in pure state, whereas the former (A) gives the same derivative (*Bz*.B) admixed with an isomeride which melts at 199–201° (*Bz*.A), and this mixture is easily separated into the components by the difference of their solubilities in alcohol. These results seem to indicate that base A[2] contains some component besides one which is common in both bases (A and B).

By hydrolysis of the benzoyl derivative melting at 199–201° (*Bz*.A) with concentrated hydrochloric acid at 150–160°, a base was regenerated which melted at 153–155°. A component of base A is thus isolated. On the other hand, the benzoyl derivative (*Bz*.B) which is common in both bases and the corresponding benzenesulphonyl derivative (m.p. 226–227°) are very resistent to hydrochloric acid and can not be hydrolyzed by the same treatment. Thus the second component which is common in both bases (A and B) can not be isolated in the form of free base, but the fact that base B gives only one benzoyl (*Bz*.B) or benzenesulphonyl derivative, leads to the conclusion that base B represents the second component in its pure state.

(1) Studies on Hydroxy-Acids and Their Derivatives. VI. Continued from this Bulletin, **12** (1937), 121.

(2) Attempts to separate the base-mixture in the form of hydrochloride, picrate or oxalate were tried but they were found to be unfavourable on account of their small solubilities in ordinary solvents.

To summarize, the existence of two bases having the same composition (m.p. 153–155° and 166–167°) is ascertained which correspond to some two optical isomerides[3] among three possible forms (active, meso and racemic) of this base.

$C_6H_5\cdot CH_2\cdot CH\cdot CH_2\cdot NH_2$
$C_6H_5\cdot CH_2\cdot CH\cdot CH_2\cdot NH_2$

2,3-Dibenzyl-tetramethylene-diamine

Free base	Benzoyl derivative	Benzenesulphonyl derivative
M.p. 153–155°	M.p. 199–201°	—
M.p. 166–167°	M.p. 280–282°	M.p. 226–227°

Uniting the present results with previous ones[1] it is established that the scheme giving 1,4-diamine and 1,2-glycol from α-hydroxy-amides is similar for the three amides, namely, amides of lactic, leucic[4] and phenyl-lactic acids.

Experimental.

The experimental procedures of the hydrogenation and the separation of reaction products are the same as described in the previous paper.[1]

Phenyl-lactamide (m.p. 113–114°), 23 g. (0.14 mol); dioxane, 60 c.c.; catalyzer, 5.0 g.; time of hydrogenation, 2 hours at 245–255°; fractionation through Widmer column after expelling off the dioxane:

I	130 – 140°	under 5 mm.	3.9 g.
II	160 – 190°	,,	4.9 g.
III	over 190°	,,	

Fraction II tends to solidify in the receiver, while fraction III remains as viscous fluid even after long standing. Considerable amount of residue was found undistilled in the flask.

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(3) Meso and racemic forms may be assigned to the above bases from the follwing reason: Measurement of optical rotation can not be carried out with both forms separately due to scarcity of the sample, but the measurement with their mixture (base A) showed no activity.

(4) As to dimethyl- and di-isobutyl-tetramethylene-diamines[1], derived from amides of lactic acid and leucic acid respectively. three isomerides are also possible and in fact, in the latter diamine, the author obtained two isomeric forms by the recrystallization of the crude base from alcohol, one melting at 60-62°, and the other at about 80°, but the latter was not reported in the previous paper because the higher melting fraction was not isolated in its pure state even in the form of its derivatives.

(A) Fraction I. (a) Neutral Part. Fraction I was separated into neutral and basic parts by extracting the acidified mixture with ether. The neutral part, after boiling with sodium hydroxide solution, was twice refractionated through Widmer column, when the main part distilled at 147–149° (uncorr.) under 6 mm. Yield, 7.2 g. from 0.42 mol of amide. It was identified as benzyl-ethylene glycol by preparing its bis-phenylurethane.

Bis-phenylurethane. Prepared from the glycol (1.0 g.) and phenyl isocyanate (2.0 g.) by heating at 120–130° for half an hour, crude urethane (3.2 g.) being crystallized by adding ligroin. It melted at 133–134° (uncorr.) or 135–136° (corr.) after recrystallization from benzene (Found: C, 70.19; H, 6.11; N, 7.22. Calculated for $C_9H_{10}O_2(OC{\cdot}NH{\cdot}C_6H_5)_2$: C, 70.73; H, 5.68; N, 7.18%). $[\alpha]_D^{25} = -13°$ (1 dm. tube; 26.5 mg. in 1.00 c.c. of alcoholic solution). When the crude sample was recrystallized from alcohol, it showed the same m.p. as above and lower melting fraction was never isolated even when seeded with a crystal of sample A (see below). $[\alpha]_D^{25} = -11°$ (25.7 mg. in 1.00 c.c.)

Supplement to Previous Paper[5]: It was already described that this glycol is also obtainable from phenyl-lactic acid when hydrogenated in the form of its acetone-compound. The sample of hydroxy-acid was the same one as was used in the present experiment and is lævo-rotatory. In that paper two forms of urethane of this glycol were mentioned and their interconvertibility by crystallization and their monotropic change by heating were described. Preparation of those urethanes were tried again and it was proved that the previous descriptions are correct. Their analyses were repeated and their optical rotations were measured. Urethane recrystallized from alcohol (sample A), m.p. 109–110° (uncorr.) (Found: C, 70.06; H, 6.15; N, 7.15%). No rotation was observed (1 dm. tube; 26.9 mg. in 1.00 c.c. of alcoholic solution). Urethane recrystallized from benzene (sample B), m.p. 132–133° (uncorr.) (Found: C, 69.96; H, 6.16; N, 7.15. Calculated for $C_9H_{10}O_2(OC{\cdot}NH{\cdot}C_6H_5)_2$: C, 70.73; H, 5.68; N, 7.18%). No rotation was observed (26.4 mg. in 1.00 c.c.).

Now, it is shown that the present urethane is active, while both forms of the former are inactive. As to the nature of the two forms of inactive urethane, following facts were observed. Sample B shows nearly the same m.p. as the active urethane and moreover mixing of them caused no appreciable depression. Mixtures (once melted and left at 110° to solidify), on heating, slightly soften below 130° and melt clearly at 131–133° (uncorr.), in every case when ratio of mixing were varied as 3:1, 2:2 and 1:3. From these behaviours of sample B it is probable that B belongs to the type of mixed crystals. If the molten mixtures are kept at room temperature, they become hard glassy masses and never tend to crystallize. Thus the formation of sample A from the molten mixture can not be realized. Sample A must be racemic compound or *dl*-mixture, and as to the last point, because of the lack of data, no decision can be given. There exists a transition point[6] between the two forms of inactive urethane. Sample A, on rapid heating, clearly melted at 110°, but when

(5) this Bulletin, **10** (1935), 531.

(6) Existence of a transition point between two inactive forms was observed in several substances, such as camphoroxime, π-chlorocamphor and methyl-mannoside. But the formation of two forms by crystallization from different solvents was not mentioned on these substances (Freudenberg, "Stereochemie," 560, Leipzig (1932).).

maintained at this temperature, it gradually resolidified and the m.p. of the resolidified mass was just the same as that of sample B.

(b) **Basic Part.** A hydrochloride, easily soluble in hot water, was obtained in small quantity. It can be recrystallized from alcohol, m.p. 271–272° (corr.). No further study on this base was made.

(B) Fractions II and III. Combined fractions were diluted with five times its volume of alcohol and concentrated hydrochloric acid was added to it. A hydrochloride gradually precipitated, the yield was not good: 4.3 g. of crude hydrochloride was obtained from 0.42 mol of the amide. After extraction with hot alcohol, the residue was dissolved in a large bulk of hot water, filtered, and was concentrated on water bath. During evaporation, a hydrochloride began to crystallize out while still hot before the solution was completely dried up. Hydrochloride (2.5 g.) thus purified was colourless and on heating showed no change of appearance up to 300°.

When the above hydrochloride was warmed with a little excess of dilute caustic soda, it changed to a crystalline free base (1.8 g. from 2.5 g. of the hydrochloride). The free base was dissolved in hot alcohol and filtered. On cooling without evaporation of the solvent, a base melting between 145° and 160° was obtained. The base which was obtained from the above filtrate by evaporation of the solvent, melted below 150°. The former fraction, after repeated recrystallization from alcohol, melted sharply at 163–164° (uncorr.) or 166–167° (corr.) (base B) and weighed 249 mg., melting point remaining unchanged on further recrystallization. The melting range of latter fraction, after repeated recrystallization, became narrower and 584 mg. of the base which melted at 140–142° (uncorr.) or 142–144° (corr.) (base A) was obtained.

(a) **Free Base Melting at 142–144° (base A).** (Found: C, 80.74; H, 9.31; N, 10.24. Calculated for $C_{15}H_{24}N_2$: C, 80.72; H, 9.02; N, 10.44%.) No rotation was observed (1 dm. tube; 25.8 mg. in 1.00 c.c. of alcoholic solution).

Benzoyl derivative melting at 199–201° (*Bz.*A). To a suspension of the base in dilute caustic soda, benzoyl chloride was added drop by drop with constant stirring. A sticky mass first formed, turned to crystallize. Benzoyl compound thus separated (660 mg. from 465 mg. of the free base) was extracted with alcohol. Benzoyl compound which was obtained from the alcoholic extract after expelling off the alcohol, melted at 195–197° (uncorr.) or 199–201° (corr.) after recrystallizations from alcohol (Found: C, 80.48; H, 6.47; N, 6.06. Calculated for $C_{15}H_{20}(NH{\cdot}CO{\cdot}C_6H_5)_2$: C, 80.60; H, 6.80; N, 5.88%).

The residue of the above extraction (149 mg.), on purification, was found to be identical in m.p. with a benzoyl compound (*Bz.*B) obtainable from the other base (base B) and it was combined with that fraction described below.

Hydrolysis. Mixture of the benzoyl compound (*Bz.* A: 85 mg.) and concentrated hydrochloric acid (10 c.c.) was heated at 150–160° in a closed vessel for four hours. After cooling, a gelatinous precipitate of hydrochloride of the regenerated base (55 mg.) was separated and it was recrystallized from water after being washed with alcohol (Found: N, 7.97. Calculated for $C_{15}H_{24}N_2{\cdot}2HCl$: N, 8.21%).

Free Base Regenerated. The base (26 mg.) which was obtained from the above hydrochloride (36 mg.) was recrystallized from alcohol and dried on porous plate over

solid caustic soda, m.p. 150–152° (uncorr.) or 153–155° (corr.) (Found: C, 80.76; H, 8.54; N, 10.58. Calculated for $C_{18}H_{24}N_2$: C, 80.72; H, 9.02; N, 10.44%).

(b) Free Base Melting at 166–167° (Base B). (Found: C, 80.53; H, 8.55; N, 10.47. Calculated for $C_{18}H_{24}N_2$: C, 80.72; H, 9.02; N, 10.44%).

Benzoyl compound melting at 280–282° (*Bz*.B). The base was benzoylated in the same way as above, 233 mg. being obtained from 150 mg. of the free base. After extraction with hot alcohol, the residue was recrystallized from glacial acetic acid, m.p. 273–275° (uncorr.) or 280–282° (corr.) (Found: C, 80.23; H, 6.94; N, 5.78. Calculated for $C_{18}H_{20}(NH{\cdot}CO{\cdot}C_6H_5)_2$: C, 80.60; H, 6.80; N, 5.88%).

Attempted Hydrolysis. The benzoyl compound is insoluble in hot concentrated hydrochloric acid and was not hydrolyzed by this reagent at 150–160°, 85% of the sample (77 mg. out of 91 mg.) being recovered unchanged after heating for four hours.

Sulphamide melting at 226–227°. The free base was added to dilute caustic soda and benzenesulphonyl chloride was added to it drop by drop. A sticky mass separated, which gradually turned to crystals on heating over water bath. After separation of the sulphamide by suction, hydrochloric acid was added to the filtrate but no precipitate was formed. The insoluble sulphamide[7] (133 mg. from 83 mg. of the free base), after acidifying with hydrochloric acid, was recrystallized from glacial acetic acid, m.p. 220–221° (uncorr.) or 226–227° (corr.) (Found: C, 65.47; H, 6.19; N, 5.12. Calculated for $C_{18}H_{20}(NH{\cdot}SO_2{\cdot}C_6H_5)_2$: C, 65.61; H, 5.91; N, 5.10%).

Attempted Hydrolysis. The sulphamide was added to a mixture of glacial acetic acid and hydrochloric acid (1:3) and was heated in sealed tube at 150–160° for four hours. The sample was not hydrolyzed: 21 mg. of sulphamide out of 25 mg. was recovered unchanged.

The present study was carried out in the Chemical Institute, Faculty of Science, Imperial University of Tokyo. The author expresses his sincere thanks to Prof. K. Matsubara for kind inspection of this paper. His best thanks are also due to Dr. Y. Takayama for constant encouragement during this study.

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(7) Yielding of sulphamide, insoluble in alkaline media, is a usual reaction of secondary amines, but the base in question, on analysis, was proved to be primary amine. It was known that some sulphamide of primary amine remained undissolved even in alkaline solution, i.e. the sodium compounds are insoluble in water, differing from the usual ones.

The Paramagnetic Isomerisation of Maleic Acid into Fumaric Acid in Aqueous Solution.

By Bunichi TAMAMUSHI and Hajime AKIYAMA.

(Received July 30th, 1937.)

R. Kuhn,[1] who demonstrated the cis-trans-isomerisation of some ethylene compounds (dimethyl ester of maleic acid and *cis*-stilbene) catalysed by paramagnetic metals, suggested as regards the mechanism of the reaction, that the absence of rotation imposed by the double bond would be overcome by the interaction between magnetically uncompensated electrons of the reacting molecule and the catalyst. Later it was shown by the present authors,[2] that the isomerisation of dimethyl ester of maleic acid can be catalysed by molecular oxygen, whose molecule is paramagnetic in spite of its even number of electrons, so that this result can be accounted for by the same mechanism. The similar view seems to be possible also in the catalysed conversion of maleic acid into fumaric acid by hydrogen ions in aqueous solution.[3]

Now in the following experiments, we attempted to ascertain the possible catalytic influence of the molecular oxygen, some paramagnetic metals and ions, on the isomerisation of maleic acid into fumaric acid in aqueous solution. It is already known that the para-ortho-hydrogen conversion in solution can be accerelated by the presence of paramagnetic molecules and ions.[4]

I.

In the first part of the following experiments, we have simply compared the amounts of the fumaric acid produced after a relapse of certain time in the reaction mixture, in the presence of paramagnetic substances with various magnetic moments. The experiments with oxygen have been always coupled with the similar experiments with nitrogen, whose molecule is diamagnetic. Thus we may be justified to conclude that the relative catalytic effects of the substances are determinable, taking into con-

(1) K. Freudenberg, "Stereochemie," 913, Leipzig (1933).
(2) B. Tamamushi and H. Akiyama, *Z. Elektrochem.*, **43** (1937), 156.
(3) C. Horrex, *Trans. Faraday Soc.*, **33** (1937), 570.
(4) L. Farkas and H. Sachsse, *Z. physik. Chem.*, B, **23** (1933), 1, 19.

sideration the role of the thermal or solvent effect, which may take place in every case under those conditions, which controlled our measurements.

The method of analysis of the reaction product which was adopted in the present work is due to Freundlich and Schikorr,[5] who studied the nature of the isomerisation of maleic acid to fumaric acid in aqueous solution in the presence of colloidal sulphur. The analysis, which is based upon the difference of solubilities of maleic acid and fumaric acid, proceeds in the following way.

Twenty c.c. of the solution to be analysed is pipetted into a 100 c.c. beaker and gently dried up on the water bath. To the residue is added 2–3 c.c. of water, which is just enough to dissolve the maleic acid in the mixture. As soon as we are sure that this process is completed, we filter the liquid with a small funnel into a small dry beaker, and then we take 1 c.c. of the filtrate for the titration with standard baryta solution, using phenolphthalein as an indicator. Thus we find out the amount of the maleic acid in the solution. The rest of the filtrate and the acids which remain in the pipette, funnel and filter paper are then transferred to the first beaker. The liquid is then boiled and titrated in the similar way as above, without newly charging the burette, so that the last reading of the baryta solution gives the total amount of the acids in the given solution. We have thus only to take the difference of the total amount of acids and the amount of the maleic acid, in order to find out the amount of the fumaric acid produced.

Since the error in the reading of burette greatly affects the result, we have constructed a special precision burette for the present purpose, which enabled us to read 0.005 c.c. accurately.

Now the amount of maleic acid which will be dissolved in the above procedure is so large, that its own volume will change the volume of the water taken, and this must be taken in account in the calculation.

If x equivalents of maleic acid are dissolved in q c.c. of water and one equivalent occupies the volume v c.c., then the volume of the solution after dissolving maleic acid will be $(q + vx)$ c.c. Assuming that 1 c.c. of the solution uses a c.c. of the normal solution, i.e. $a\frac{f}{1000}$ acid-equivalents, we have for $(q + vx)$ c.c. solution $(q + vx)\frac{af}{1000}$ acid-equivalents, where f denotes the factor of the normal solution. So that we get the equation:

(5) H. Freundlich and G. Schikorr, *Kolloid-Beihefte*, **22** (1926), 1.

$$(q+vx)\frac{\alpha f}{1000} = x\,,$$

from which we obtain x.

The equivalent volume v was in our case determined by special experiments with the following results: $v = 39.1$ c.c. at 10°C. and $v = 40.0$ c.c. at 14°C.

The control experiments were made with a known mixture of the two acids, which contained namely 0.058 g. of fumaric acid and 1.102 g. of maleic acid and consequently just 5.00% of fumaric acid. The results obtained are given in Table 1.

Table 1.

No. of Exp.	Fumaric Acid (%)		Error (%)
	theor.	exp.	
1	5.00	4.62	7.6
2	5.00	4.85	3.0
3	5.00	5.07	1.4
4	5.00	4.67	6.2
			Mean 4.6

The accuracy of the analysis can therefore be estimated to about 5 percent in the mean.

A small quartz or Pyrex flask with reflex condenser, into which 30–50 c.c. half molar solution of maleic acid had been introduced, was put in a boiling water bath thermostat, temperature of which was regulated electrically within ± 0.2°, during the reaction time. The upper part of the flask was covered with an aluminium foil to protect the solution from light, which is well known to have an influence on the rate of the isomerisation.

In the case of measurements with oxygen or nitrogen, the gas was bubbled through the solution under a constant pressure during the reaction to ensure the solution to be saturated with the gas. By the method of Kautzky and Thiele[6] we prepared the nitrogen used in the experiment, which was completely free from oxygen.

In the following series of experiments with paramagnetic ions, a small amount of sulphates of divalent metals or nitrates of trivalent metals was added to the solution, the concentration of the salt being 5 millimolar per litre in each case, so that any secondary chemical change in the solution could be excluded.

The platinum black and the palladium black were prepared by the method of Mond, Ramsay, and Shields,[7] which exhibited high catalytic

(6) H. Kautzky and H. Thiele, *Z. anorg. allgem. Chem.*, **152** (1926), 342.
(7) L. Mond, W. Ramsay, and J. Shields, *Phil. Trans.*, **186** A (1895), 661.

activity in burning hydrogen. The chemicals used were the purest ones of either Merck or Kahlbaum.

The results obtained are summarized in the following tables, in which the values of magnetic moments or of magnetic susceptibilities of the catalysts are too noted. The adopted values of the fumaric acid produced in Table 3 and 4 are the mean of two or three measurements, since they fluctuate considerably within the error of the analysis.

Table 2. Conc. of Maleic Acid = 0.5 mol/l. Temp. = 99.5°C. Reaction Time = 10 hours.

No. of Exp.	Fumaric Acid produced (%) in presence of	
	O_2	N_2
1	8.7	5.1
2	9.1	5.7
3	9.0	6.1

Table 3. Conc. of Maleic Acid = 0.5 mol/l. Temp. = 99.5°C. Reaction Time = 10 hours.

Ion (5 millimol/l.)	Fumaric Acid produced (%)	Magnetic Moment[8] in Bohr Magneton Number
Zn^{2+}	6.5	0
Cu^{2+}	7.7	3.53
Mn^{2+}	8.6	5.92
Fe^{2+}	8.9	6.54
Co^{2+}	11.1	6.56
Ni^{2+}	11.3	5.56
Pr^{3+}	9.5	3.62
Nd^{3+}	10.1	3.68
Er^{3+}	11.1	9.70

Table 4. Conc. of Maleic Acid = 0.5 mol/l. Temp. = 99.5°C. Reaction Time = 10 hours.

Catalyst (0.03 g. in 30 c.c. solution)	Fumaric Acid produced (%)	Specific Mass Susceptibility $\chi \cdot 10^6$
Pt-black	8.8	1.1
Pd-black	10.7	5.8

As we see in Table 2, the amount of the fumaric acid produced in the presence of oxygen evidently exceeds that produced in the presence of nitrogen. The isomerisation must have been accerelated by the non-homogeneous magnetic field of the O_2-molecules in the process of collision. A more or less considerable isomerisation is also observed in the presence of the paramagnetic ions or metals, where a certain parallelism being displayed between the fumaric acid produced and the magnetic moment of the catalyst. We dare not, however, formulate quantitatively the relation between them, in order to make use of it in further discus-

(8) J. H. van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford (1932).

sions, for our experiments have not yet so far advanced as to determine the velocity constant of the reaction in each case, whereas an interesting quantitative treatment has been performed in the case of the para-ortho-hydrogen conversion in solution catalysed by paramagnetic ions.[9]

The concentration of the paramagnetic ions seems to have in general no remarkable effect on the rate of the isomerisation, as is shown in Table 5, although a slight increase of the reaction product with the ion-concentration is noticed in the case of Nd^{3+}. The effect of the anion has been examined with the salts of the same cation in the same molar concentration and it was found to be negative, as is given in Table 6.

Table 5. Conc. of Maleic Acid = 0.5 mol/l. Temp. = 99.5°C. Reaction Time = 10 hours.

Salt	Concentration of Salt (millimol/l.)	Fumaric Acid produced (%)
$NiSO_4$	5	11.3
	10	11.4
	20	11.4
$Nd(NO_3)_3$	5	9.7
	10	10.7
	20	12.7

Table 6. Conc. of Maleic Acid = 0.5 mol/l. Temp. = 99.5°C. Reaction Time = 10 hours.

Salt (5 millimol/l.)	Fumaric Acid produced (%)
$NiCl_2$	11.9
$NiSO_4$	11.9
$Ni(NO_3)_2$	12.5

It is of interest to compare these results with those, which have been obtained by Farkas and Sachsse in the para-ortho-hydrogen conversion.

The effect of water itself as a solvent on the isomerisation of maleic acid in solution, which will be brought about by the nuclear moment of the protons of water molecules and which may probably take place as in the case of the para-ortho-hydrogen conversion,[10] can not, however, be brought out so long as the reaction is not studied in other solvents.

II.

The next step in our studies was to get some informations about the nature of the reaction under consideration, and for this purpose we have made kinetic measurements, which however concern only the reaction in the presence of paramagnetic oxygen molecules on the one hand, and on the other the reaction in the presence of diamagnetic nitrogen molecules.

(9) Farkas and Sachsse, *Z. physik. Chem.*, B, **23** (1933), 19; H. Sachsse, *Z. Elektrochem.*, **40** (1934), 531.

(10) Farkas and Sachsse, *Z. physik. Chem.*, B, **23** (1933), 14.

The rate of the reaction was determined in both cases at different temperatures, namely at 80°, 90° and 100°C., while the reaction vessel was put in an electrically regulated oil thermostat with the temperature variation within ± 0.1°.

The reaction mixture was taken from time to time to be analysed in the manner as described above. The results are tabulated in Table 7 and 8, where k denotes the unimolecular velocity constant. Although this constant shows some irregular variations, the correctness of the assumption of unimolecularity can be accepted on the ground of the experiment with varied initial concentrations of the reacting substance, the results of which being shown in Table 9.

Table 7. Conc. of Maleic Acid = 0.5 mol/l. Saturated with O_2.

Temp. (°C.)	Time (hours)	Fumaric Acid produced (%)	$k \cdot 10^6$ (sec.$^{-1}$)
80	15	3.2	0.60
	25	5.4	0.62
	40	9.9	0.72
			Mean 0.65
90	10	5.3	1.52
	23	7.8	0.98
	35	11.9	1.00
			Mean 1.17
100	10	9.0	2.62
	17	11.0	1.90
	20	11.8	1.73
			Mean 2.04

Table 8. Conc. of Maleic Acid = 0.5 mol/l. Saturated with N_2.

Temp. (°C.)	Time (hours)	Fumaric Acid produced (%)	$k \cdot 10^6$ (sec.$^{-1}$)
80	15	2.1	0.39
	25	3.7	0.42
	40	6.1	0.44
			Mean 0.42
90	10	3.4	0.97
	23	5.4	0.68
	35	7.0	0.58
			Mean 0.74
100	10	6.1	1.75
	14	7.1	1.47
	23	8.1	1.01
			Mean 1.41

Table 9. Maleic Acid Solution, saturated with O_2. Reaction Time = 15 hours.

Initial Conc. of Solution (mol/l.)	Fumaric Acid produced in millimol/l. after			$k \cdot 10^6$ (sec.$^{-1}$)
	5 hours	10 hours	15 hours	
0.25	0.0013	0.0023	0.0030	2.53
0.5	0.0031	0.0045	0.0070	2.75
1.0	0.0069	0.0092	0.0113	2.87
2.0	0.0126	0.0176	0.0206	2.73

Of the values of the fumaric acid which was produced in the above experiments at lower temperatures than 100°, due corrections were made

according to the circumstance, that in the reaction mixture, which was used for the analysis, the reaction would proceed, during the process of evaporation, further than the proper stage of the reaction. These corrections are not more than one percent, which was proved by special experiments and also by calculations from the data obtained at 100°.

From the data in Table 7 and 8, it is again obvious that the isomerisation proceeds remarkably quicker in the presence of oxygen than in the presence of nitrogen. The variation of the velocity constant with temperature follows the equation of Arrhenius:

$$\ln k = \ln Z - \frac{E}{RT},$$

as is illustrated in Fig. 1. We obtain thus for the reaction with oxygen the equation:

$$\ln k = 6.75 - \frac{14600}{RT},$$

and for the reaction with nitrogen:

$$\ln k = 7.96 - \frac{15800}{RT},$$

where k being measured in sec.$^{-1}$

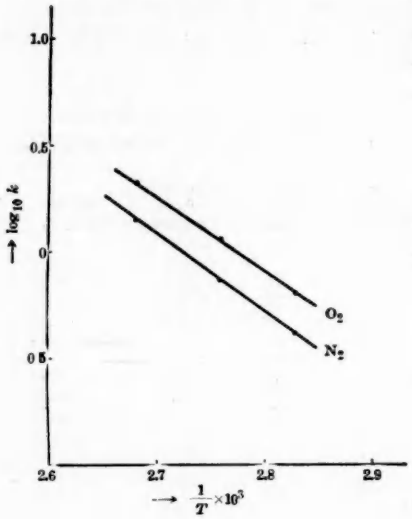

Fig. 1.

The energy of activation is thus lowered in the presence of oxygen, and this accounts for the catalytic action of molecular oxygen. The comparatively low values of ln Z are due to the slowness of the reaction in question.

It would be rather accidental that the energy of activation obtained above in the reaction with nitrogen i.e. 15.8 Cal. per mol is coincident with that, which was found by Höjendahl[11] for the isomerisation of maleic acid into fumaric acid in fused state, while Kistiakowsky and Nelles[12] found 26.5 Cal. per mol for the isomerisation of dimethyl maleic acid to dimethyl fumaric acid in gaseous state.

(11) K. Höjendahl, *J. Phys. Chem.*, **28** (1924), 758.

(12) G. B. Kistiakowsky and Nelles, *Z. physik. Chem.*, Bodenstein-Festband (1931), 369.

We hope that we can enter into further discussions on this subject, when we shall make reports of the studies of kinetics, which are now under way in our laboratory, concerning the isomerisation of dimethyl ester of maleic acid in gaseous phase in presence and in absence of molecular oxygen.

Summary.

It has been demonstrated that the isomerisation of maleic acid into fumaric acid in aqueous solution is accerelated by the presence of molecular oxygen, platinum black, palladium black, and various paramagnetic ions, where the isomerisation being probably effectuated by the non-homogeneous magnetic fields of the catalysts in the collision.

The isomerisation of maleic acid to fumaric acid in aqueous solution has been kinetically studied both in the presence of paramagnetic oxygen molecules and in the presence of diamagnetic nitrogen molecules, and the energy of activation of the reaction has been calculated. The lower energy of activation in the reaction with oxygen accounts for the catalytic action of the oxygen molecules.

We are much indebted to the Nippon Gakujutsu Shinkokai for a grant.

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Absorptionsspektren von Metallkomplexsalzen des 2,2′-Dipyridyls. I.

Von Kazuo YAMASAKI.

(Eingegangen am 2. August 1937.)

Seit der Auffindung des 2,2′-Dipyridyls durch F. Blau, haben zahlreiche Arbeiten[1] über die Komplexsalze des Dipyridyls mit verschiedenen Metallen schon erschienen, aber keine spektrochemische Untersuchung derselben ist anbei geschehen. In vorliegender Arbeit teile ich die Messergebnisse der Absorptionsspektren der Komplexsalze $[M(Dip)_3]Cl_2$[3] mit, hierbei bedeuten *Dip* Dipyridyl und M zweiwertige Kupfer, Zink, Eisen, Nickel und Kobalt, sowie dreiwertiges Kobalt.

Experimentelles. Das 2,2′-Dipyridyl wurde aus Pyridin und wasserfreiem Eisenchlorid im Autoklave dargestellt.[2] Die Komplexsalze wurden meist durch Mischung der Lösungen des betreffenden Metallchlorids (1 Mol) und des Dipyridyls (3 Mol) hergestellt.[3] Sie sind beständig und löslich in Wasser und Alkohol. Im Falle der alkoholischen Lösung wurden die Absorptionsmessungen auch bis tiefen Temperaturen ($-60° \sim -70°$C.) ausgedehnt.

Die Absorptionsspektren wurde mit Hilfe von Quarzspektrograph (Hilger E2) nach der Hartley-Balyschen Methode aufgenommen. Der beobachtete Spektralbereich reichte von 220 mμ bis 850 mμ und als Lichtquelle dienten, je nach der Messbedingungen, Eisenbogen, Glühlampe und Wasserstofflampe mit Quarzfenster. Für die Versuche bei Zimmertemperatur ($+15°$) wurde ein gewöhnliches Balyrohr benutzt, aber die Messungen bei tiefen Temperaturen wurden mit einem speziellen Balyrohr von verschmolzener Quarz[4] ausgeführt (Abb. 1). Die Temperatur

(1) F. Blau, *Ber.*, **21** (1888), 1077; *Monatsh.*, **10** (1889), 372; **19** (1898), 647; G. T. Morgan und F. H. Burstall, *J. Chem. Soc.*, **1930**, 2594; **1931**, 2213; **1934**, 965; P. Pfeiffer, K. Quehl und F. Tappermann, *Ber.*, **64** (1931), 2667; *Z. anorg. Chem.*, **215** (1933), 273; G. A. Barbieri und A. Tettamanzi, *Atti accad. Lincei*, **15** (1932), 877; **16** (1933), 44; **20** (1934), 273; F. Rosenblatt und A. Schleede, *Ann.*, **505** (1933), 51; F. M. Jaeger und J. A. van Dijk, *Z. anorg. Chem.*, **227** (1936), 273; A. Simon, *Z. anorg. Chem.*, **230** (1937), 160.

(2) F. Hein und H. Schwedler, *Ber.*, **68** (1935), 681.

(3) F. M. Jaeger und J. A. van Dijk, *Z. anorg. Chem.*, **227** (1936), 273.

(4) Y. Shibata und K. Harai, *J. Chem. Soc. Japan*, **56** (1935), 1.

der Lösung wurde mit einem Thermoelement von Kupfer-Konstantan gemessen und die Temperaturänderung während eines Versuches im Sichtbaren (20 Min.) war ca. ± 5° bei − 65°. Im Ultraviolett wurde die photographische Aufnahme bei Zimmertemperatur mit der Wasserstofflampe ausgeführt, wobei die mehrstündige Belichtung immer nötig war, infolge ihrer schwachen Lichtstärke; also, bei tiefen Temperaturen, konnte man diese Lichtquelle nicht benutzen, weil die Lösungstemperatur so lange Zeit keineswegs konstant erhalten werden kann. Infolgedessen wurden die Absorptionsmessungen bei tiefen Temperaturen nur in sichtbarem Gebiet beschränkt, indem die Glühlampe als die Lichtquelle in Verwendung gebracht wurde.

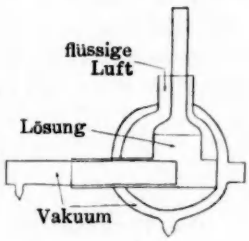

Abb. 1.

Messergebnisse. Dipyridyl: Farblose Kristalle. Es wurden die Lösung in Wasser und Hexan von Konzentration 1/5000 Mol untersucht. Das benutzte Hexan wurde nach Henri[5] gereinigt (Abb. 2,[6] Kurve 5, 6).

in Wasser (15°), λ_{max} in mμ: 280, 230.
in Hexan (15°), ,, : 280, 244+235.

In Hexan ist die zweite Bande nach längeren Wellen um 10 mμ verschoben und teilte sich in zwei schmalen Banden.

$[Cu(Dip)_3]Cl_2$: Blauviolette Tafeln. Wie andere Kupferkomplexsalze, zeigte dieses Salz auch keine Absorptionsbande im Sichtbaren, aber nur eine breite Bande im Ultraviolett ist beobachtet (Abb. 2, Kurve 1, 2, 3).

in Wasser (15°), λ_{max} in mμ: 298.
in Alkohol (15°), ,, : 293.
Konzentration: 1/50−1/10000 Mol.

$[Zn(Dip)_3]Cl_2$: Farblose Blättchen. In wässriger Lösung hat es einige Absorptionsbanden bei 307, 295 und 240 mμ (Abb. 2, Kurve 4).

$[Ni(Dip)_3]Cl_2$: Dunkelrote Tafeln. Konzentration: 1/20−1/10000 Mol[7] (Abb. 3).

(5) V. Henri, *Bull. soc. chim. biol.*, **6** (1924), 299.

(6) Auf der Ordinate wurde die Logarithmen der Schichtdicke (mm.) der Lösung entsprechend 1/10000 Mol aufgetragen.

(7) Bei −65° war die untersuchte grösste Konzentration der Lösung 1/40 Mol.

in Wasser (15°), λ_{max} in mμ: 750, 508, 308+296, 245.
in Alkohol (15°), ,, : 750, 520, 309+296, —[8].
,, (−65°), ,, : 520, 430.

In Alkohol trat die Verschiebung der Banden nach Rot auf und bei −65° trat eine neue Bande in Erscheinung. Vergleicht man die Lage der Absorptionsmaxima im Sichtbaren mit den der anderen Nickelhexamminsalze,[9] so zeigt sich die folgende Werte:

$[Ni(NH_3)_6]Cl_2$, $1/\lambda$: 170, 275.
$[Ni(en)_3]Cl_2$, ,, : 180, 290.
$[Ni(Dip)_3]Cl_2$, ,, : 197 (508 mμ).

Die Verschiebung der erste Bande nach kürzeren Wellen tritt mit zunehmender Molekulargrösse der Liganden. Die zweite Bande bei 275 in $1/\lambda$ fehlt beim Dipyridylkomplexsalz, aber es besitzt die Knicke der Absorptionskurve bei 410–330 mμ ($1/\lambda$ = 244–303).

$[Fe(Dip)_3]Cl_2$: Weinrotes Blättchen. Es wurden die Lösungen von Konzentration 1/2000–1/10000 Mol untersucht (Abb. 4).

in Wasser (15°), λ_{max} in mμ: 500, 352, 299+290, 247.
in Alkohol (15°), ,, : 510, 350, 300+290.
,, (−60°), ,, : 530, 420, 400.

In Alkohol trat die Verschiebung der erste Bande nach Rot auf und bei −60° zeigte das Spektrum zwei neue schmale Absorptionsbande.

$[Co(Dip)_3]Cl_2$: Komplexsalz des zweiwertigen Kobalts. Gelbe Schuppen. Konzentration: 1/50–1/10000 Mol (Abb. 5, Kurve 1, 2, 3).

in Wasser (15°), λ_{max} in mμ: 305+295, 243.
in Alkohol (15°), ,, : 307+295.

$[Co(Dip)_3]Cl_3$: Komplexsalz des dreiwertigen Kobalts. Gelbbraune Kristalle. Durch anodische Oxydation hergestellte Kobaltisulfat wurde mit Dipyridyl versetzt und das so erhaltene Tridipyridylkobaltisulfat wurde mittels Bariumchlorids in das Chlorid umgesetzt. Es ist ziemlich schwer löslich in Alkohol, aber leicht in Wasser. Konzentration: 1/50–1/10000 Mol (Abb. 5, Kurve 4, 5).

in Wasser (15°), λ_{max} in mμ: 450, 319+307.
in Alkohol (15°), ,, : 320+310.

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(8) Die bei 250 mμ beginnende Absorption von Alkohol überdeckt diese Bande und macht die Messung unmöglich.
(9) Y. Shibata, *J. Chem. Soc. Japan.*, **39** (1918), 661; *J. Coll. Sci., Imp. Univ. Tokyo*, **41** (1918), Art. 6, S. 23.

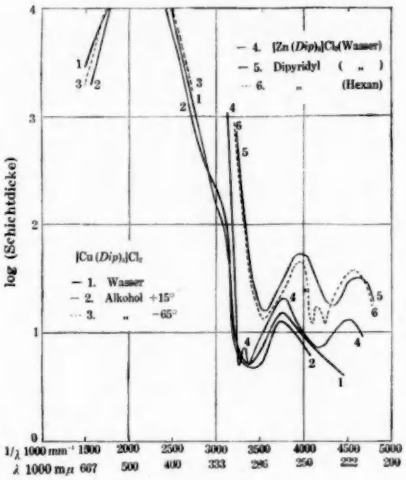

Abb. 2.

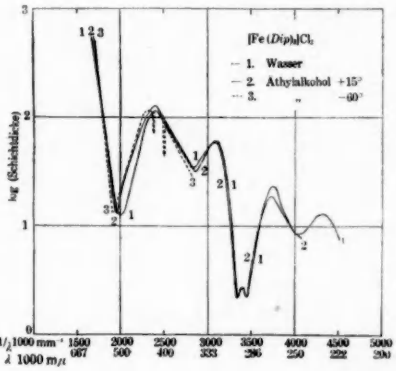

Abb. 4.

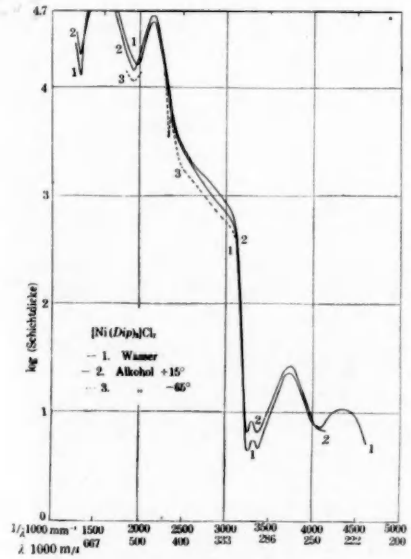

Abb. 3.

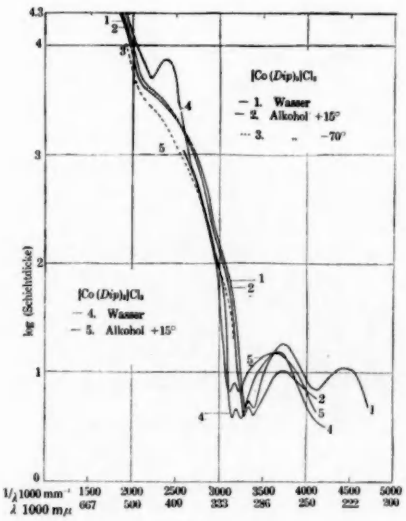

Abb. 5.

Die erste Absorptionsbande im Sichtbaren der Kobaltihexamminsalze verschiebt sich nach kürzeren Wellen mit dem zunehmenden Molekulargrösse der Liganden.

$[Co(NH_3)_6]Cl_3$: 475 mμ.[10]
$[Co(en)_3]Cl_3$: 467 mμ.
$[Co(Dip)_3]Cl_3$: 450 mμ.

Die Differenz zwischen Kobalto- und Kobalti-salz liegt darin, dass die Absorptionsbande im Sichtbaren fehlt beim Kobaltosalz, während die ultraviolette Bande von Kobaltisalz um 15 mμ nach längeren Wellen als die des Kobaltosalzes liegt.

Alle Komplexsalze, die Dipyridyl in koordinativer Bindung enthalten, sind durch zwei Banden im Ultraviolett charakterisiert, deren Formen sich der des Dipyridyls stark ähneln. Die eine von diesen zwei Banden liegt bei ca. 300 mμ, die andere bei 245 mμ, von denen die erste, in allen Fällen mit Ausnahme von Kupfersalz, die Spaltung in zwei schmalen Banden beobachtet wurden. Die zweite Bande bei 245 mμ ist nicht vorhanden bei Kupfer- und Kobaltisalz. Zwar diese zwei Bande treten sich erst bei grosser Verdünnung (1/8000–1/10000 Mol) auf, aber es scheint mir, dass sie durch die Zersetzung (oder Hydrolyse) des Komplexsalzes und durch die Befreiung des Dipyridyls nicht verursacht werden, denn ihrer Lagen stark von den des freien Dipyridyls abweichen. Sie müssen den Dipyridylmoleküle in koordinativer Bindung zugeordnet werden.

Zusammenfassung.

Die Absorptionsspektren der wässrigen und alkoholischen Lösungen von Tridipyridylkomplexsalze des zweiwertigen Kupfers, Zinkes, Nickels, Eisens, und Kobalts, sowie des dreiwertigen Kobalts wurden untersucht. In der alkoholischen Lösungen wurde die Messung auch bei tiefen Temperaturen wie $-60° \sim -70°$ ausgeführt. In Alkohol sind einige Absorptionsbanden im Sichtbaren nach längeren Wellen verschoben, aber die ultraviolette Banden sind durch Lösungsmittel wenig beeinflusst. Ausserdem, bei tiefen Temperaturen, wurden einige schmale Banden beobachtet.

Es sei mir gestattet, Herrn Prof. Yuji Shibata für seine freundliche Anleitung und Ratschläge bei der Ausführung dieser Arbeit meinen herzlichen Dank auszusprechen.

Chemisches Institut, Naturwissenschaftliche Fakultät,
Kaiserliche Universität zu Tokyo.

(10) J. P. Mathieu, *Bull. soc. chim.*, [5], **3** (1936), 647.